CERAMIC FOAM-SUPPORTED PEROVSKITES AS CATALYSTS FOR COMBUSTION OF METHANE

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Methane combustion in the presence of various types of perovskites supported on ceramic foams has been studied with respect to the CO and NO_x formation. The effect of the catalyst composition and of the air-to-methane ratio on the CO and NO_x concentration has been evaluated for different burner capacities.

Key words: Catalytic combustion; Ceramic foam; Perovskites.

Catalytic combustion of methane has become a very frequently studied oxidation reaction as large amounts of NO_x, which are formed in flame combustion, deteriorate the environment. Oxidation of methane in a catalytic burner proceeds at rather high reaction temperatures (1 100–1 350 °C), at which noble metals as active components of the catalysts are not stable enough. In our previous study[1] we analyzed catalytic properties of ceramic foams covered with a layer of alumina and various combinations of platinum and lanthanum. We found that the activity of the platinum catalyst decreased during the reaction, probably due to sintering of platinum particles and/or their volatilization. Information from literature[2–4] indicates that perovskites can be active in methane combustion and, at the same time, sufficiently stable at high temperatures.

The aim of our work was to prepare various types of perovskites (supported on ceramic foams), to use them in a catalytic burner of methane, to evaluate their ability to oxidize methane with respect to the NO_x and CO formation and to follow their thermal stability at high reaction temperatures.

EXPERIMENTAL

Catalysts and Chemicals

The ceramic foam (support) was supplied by Chemopetrol Litvinov, Czech Republic. Its bulk density was 560 kg/m^3 and external surface area 650 m^2/m^3. Mean diameter of the channels was about 4 mm the geometric structure of the foam can be seen in Fig. 1. Composition of the foam is following

(mole %): 51.5 Al, 25.6 Si, 7.0 Zr, 7.0 Mg, 3.0 Ca, 0.9 K, 2.3 Na, 0.7 Ce, the rest is Fe, Mn and other elements.

The catalysts were prepared by wash-coating of ceramic foams in the form of cylinder (diameter 6 cm, height 2 cm) with alumina sol stabilized with lanthana. The sol was prepared by mixing aluminum hydroxide with nitric acid and lanthanum nitrate for alumina stabilization. After drying and calcining at 800 °C for 1h, the wash-coated foams were impregnated with mixed solutions of La, Co, Ni or Ba nitrates and Sr, Fe, Mn chlorides or chloroplatinic acid in such a ratio, so that perovskites of required composition would be obtained after the calcination at 800 °C for 1h. Theoretical amount of wash-coat located on the foam surface was 5 wt.% and the amount of perovskite 1 wt.%. The survey of the catalysts prepared together with the actual amounts of wash-coat and active material (determined from a change in the weight) is given in Table I.

Characterization of the Catalysts

Electron microprobe technique (JEOL, Japan) equipped with a computation unit EDAX was used for evaluation of the catalyst composition.

Surface properties of the catalysts prepared were characterized by temperature-programmed desorption of oxygen. Sample (0.05 g) was calcined in a stream of helium at 900 °C (the rate of temperature increase was 20 K/min), an excess of oxygen was dosed to the sample at 800 °C and at 20 °C, the physically adsorbed oxygen was removed by a stream of helium and, after reaching a steady-state value, temperature-programmed desorption of oxygen was started (rate of temperature increase 20 K/min). Calibration made it possible to obtain quantitative data on oxygen desorption.

Catalytic Combustion Procedure

The catalyst activity was evaluated in a catalytic burner schematically depicted in Fig. 2. The following procedure was applied for catalyst testing: A catalyst was placed in a burner, flows of methane and air were adjusted and the resulting mixture of a required air-to-methane ratio was ignited. After the stabilization of process parameters or after every change of flow parameters, CO and NO_x concentrations were measured by gas analyzer IMR 3000P (Germany) after 1 h of the burner work. The NO_x concentration was also measured with a VAMET instrument (Vanicek, Praha, Czech Republic), the CO concentration with an IREX instrument (CHEZA, Litvinov, Czech Republic) and the O_2 concentration with a Permolyt 2 instrument (VEB Junkalor, Dessau, Germany). The procedure ensured
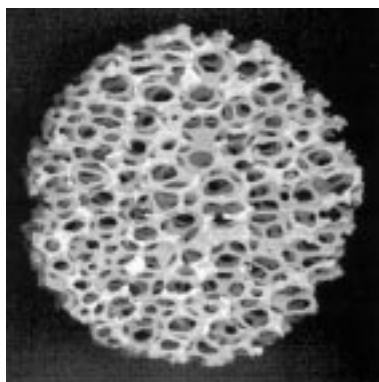

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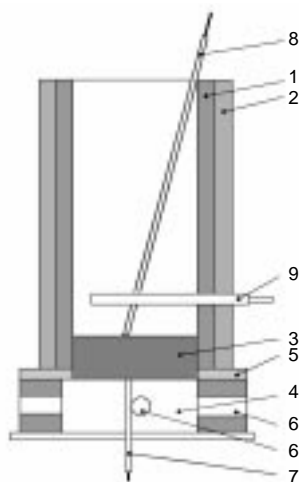Geometric structure of a ceramic foam used as the catalyst support

reproducible conditions of methane combustion in experiments. In order to avoid high-temperature destruction of the catalysts or a destruction of the IMR gas analyzer, the experiments were stopped at the moment when catalyst temperature reached 1 200 °C or the CO concentration reached 1 000 ppm. Details of the catalytic burner and the procedure are given elsewhere[5]. In addition to the CO and NO_x concentrations, temperature of the catalyst sample was measured during the experiments by Pt–PtRh thermocouples.

TABLE I
Composition of prepared samples

Active components		Wash-coating of foams with $Al_2O_3 + La_2O_3$, wt.%
Type	wt.%	
Foam	0	0
$LaNiO_3$	1.1	3.5
$LaCoO_3$	0.8	4.8[a]
$LaMnO_3$	1.2	5.0
$LaFeO_3$	1.4	5.0
$La_{0.8}Sr_{0.2}CoO_3$	1.4	4.3
$La_{0.6}Sr_{0.4}CoO_3$	1.1	3.7
$La_{0.4}Sr_{0.6}CoO_3$	1.2	2.6
$BaPtO_3^A$	0.3	3.7
$BaPtO_3^B$	1.2	2.6

[a] Ceramic foam covered with La_2O_3 only.

FIG. 2
Scheme of the catalytic burner. **1** Ceramic tube, **2** thermal insulation, **3** catalyst, **4** combustion space, **5** quartz wool, **6** methane feed, **7, 8** Pt–PtRh thermocouples, **9** sampling place

RESULTS AND DISCUSSION

In the presence of ceramic foams modified by perovskites ($LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $LaNiO_3$, $LaMnO_3$, $LaFeO_3$, or $BaPtO_3$), the amounts of NO_x and CO in the products of methane combustion were determined for various air-to-methane ratios and methane throughputs.

NO_x Concentration

Similarly to the previous findings[1] with metal oxides or platinum supported on ceramic foams, the NO_x concentration in the flue gases decreased non-linearly with increasing air excess λ and ranged from 3 to 150 ppm for all perovskite catalysts. In order to evaluate catalytic properties of the perovskites used, the NO_x concentrations in the effluent were compared at a chosen value of the air-to-methane ratio (1.95) and at the same methane throughput (150 l/h) – see Table II. The highest value of the NO_x concentrations (*ca* 125 ppm) was observed with the $LaFeO_3$ perovskite and the lowest (*ca* 12–17 ppm) with the $BaPtO_3$ and $LaNiO_3$ catalysts. The different abilities of the perovskites to catalyze reaction between nitrogen and oxygen could be accounted for the different NO_x values.

TABLE II
The CO and NO_x concentrations, ppm, in flue gases obtained with various types of perovskites supported on ceramic foams at the air-to-methane ratio $\lambda = 1.95$ and various methane throughputs Q, l/h

Sample	wt.%	Q, l/h	CO	NO_x
LaCo	0.8	150	22	32
LaMn	1.2	150	26	25
LaNi	1.1	150	20	17
		70–390	120	17
		350	1 000	3
LaFe	1.4	150	12	125
		250	10	85
BaPt	1.2	50–140	8	12
LaSrCo[a]	1.2	150	2	71
		250	2	58
		300	0	46

[a] $La_{0.8}Sr_{0.2}CoO_3$.

CO Concentration

The CO concentrations in the flue gases were not so straightforwardly dependent on the air excess λ as the NO_x ones. The CO concentrations varied in the range from 1 000 ppm to 0 ppm depending on the catalyst and reaction conditions used. In the presence of all perovskites, a minimum of the CO concentration was observed when λ was in the range of values 1.7–2.0. For the purpose of catalyst comparison, we determined the CO concentrations in the effluent at $\lambda = 1.95$ and methane throughput $Q = 150$ l/h. The lowest CO concentrations, *i.e.* the most active catalyst in the complete oxidation of methane to CO_2, were found with the $La_{0.8}Sr_{0.2}CoO_3$ and $BaPtO_3$ catalysts. The lowest oxidation activity, *i.e.* the highest CO concentrations in the gas effluent, was observed with the $LaMnO_3$ perovskite (26 ppm).

As mentioned previously, with metal oxides as oxidation catalysts, we demonstrated[1] non-linear dependence of the NO_x concentration on λ in the range from 1.2 to 2.5, and a more complex dependence of the CO concentration on the increasing λ value. The dependence showed a local minimum, the position of which differed with the type of catalyst used but for all catalysts it was in the range of $\lambda = 1.7$–1.9. With the catalysts based on perovskites, similar dependencies of the CO and NO_x concentrations on the air-to-methane ratio λ were found. Typical dependencies of both compounds on the λ value (1.75–2.75), together with the catalyst temperature are given in Fig. 3 (for the 0.3 wt.% $BaPtO_3$ perovskite on the ceramic foam and the burner capacity of 169 W/cm^2). Evidently, the trend of the catalyst temperature corresponds to that of the NO_x concentration. With increasing an air excess, the theoretical adiabatic temperature decreases[1] and that is why the NO_x concentration decreases.

If the burner capacity was decreased to 84 W/cm^2, all three dependencies (CO, NO_x, temperature) showed similar trends (Fig. 4) as those showed in Fig. 3, with one exception: The range of the air-to-methane ratio in which the burner combusted methane
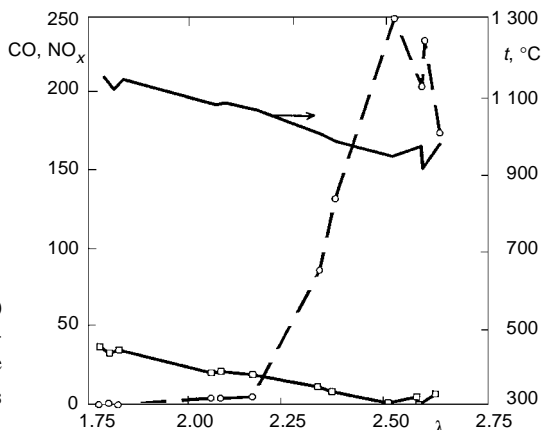

FIG. 3
Dependences of the CO (○) and NO_x (□) concentrations (in ppm) and catalyst temperature (solid line) on the air-to-methane ratio λ obtained with the 0.3 wt.% $BaPtO_3$ catalyst and burner capacity 169 W/cm^2

continuously, was increased – from the value of 1.75 to 6.75. At the highest value of the air excess (6.75), the catalyst temperature decreased to 560 °C. Even at such low temperature, the catalyst was able to combust methane producing relatively low concentrations of CO. Hence, a high catalyst activity makes complete oxidation of methane possible at low reaction temperature, and at high air-to-methane excess. For this reason we can suggest the range of the air-to-methane ratio in which the burner works continuously and reliably as a measure of the catalyst activity. The dependencies found for the perovskite catalysts working at various burner capacities are depicted in Fig. 5. We have found that with increasing output of the burner (W/cm^2), the interval of the air excess became narrower for all catalysts examined. The air excess interval λ in which the catalyst worked is closely associated with the temperature of catalyst surface. In Fig. 5, two ranges of the air-to-methane ratio are shown:

a) First λ interval (denoted by ❒) is an interval in which the catalyst in the catalytic burner worked reliably and continuously (the combustion temperature is restricted by the value of 1 200 °C and by a catalyst temperature at which the CO concentration in the effluent is lower than 1 000 ppm, so that the IMR 3000P gas analyzer would not be damaged).

b) Second λ interval (denoted by ∎) shows limits within which the content of NO$_x$ was lower than 50 ppm and, at the same time, the CO concentration was lower than 100 ppm.

From Fig. 5 follows that the oxidation activities of the pure ceramic foam, the LaNiO$_3$ and LaCoO$_3$ perovskites are very similar and rather low. The La$_x$Sr$_y$CoO$_3$ perovskites are much more active than the catalysts mentioned above and almost so active as the BaPtO$_3$ perovskite of the same concentration on the support. Of the whole set of the La$_x$Sr$_y$CoO$_3$ perovskites tested, the La$_{0.8}$Sr$_{0.2}$CoO$_3$ catalyst was the most active.

The decrease in the BaPtO$_3$ perovskite concentration in the catalyst from 1.2 wt.% to 0.3 wt.% led to a great increase in the catalyst activity. Very probably, a lower perov-
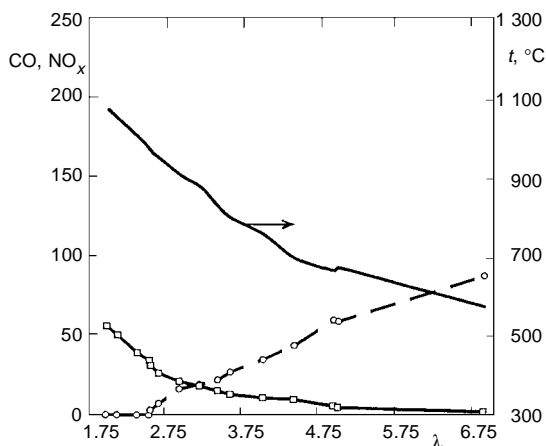

FIG. 4
Dependences of the CO (○) and NO$_x$ (❒) concentrations (in ppm) and catalyst temperature (solid line) on the air-to-methane ratio λ obtained with the 0.3 wt.% BaPtO$_3$ catalyst and burner capacity 84 W/cm^2

skite concentration on the support surface caused a formation of smaller catalyst particles, better dispersion of active component on the catalyst surface and, at the same time, an increase in catalyst activity. Obviously, in the catalysts with higher perovskite concentrations not all catalyst particles are fully accessible to the reaction components. Lower dispersion of active component can be expected if a low-surface area support is used for the catalyst preparation.

TABLE III
Characteristic parameters obtained by TPD of oxygen from the samples of some perovskites mixed with wash-coated ceramic foams

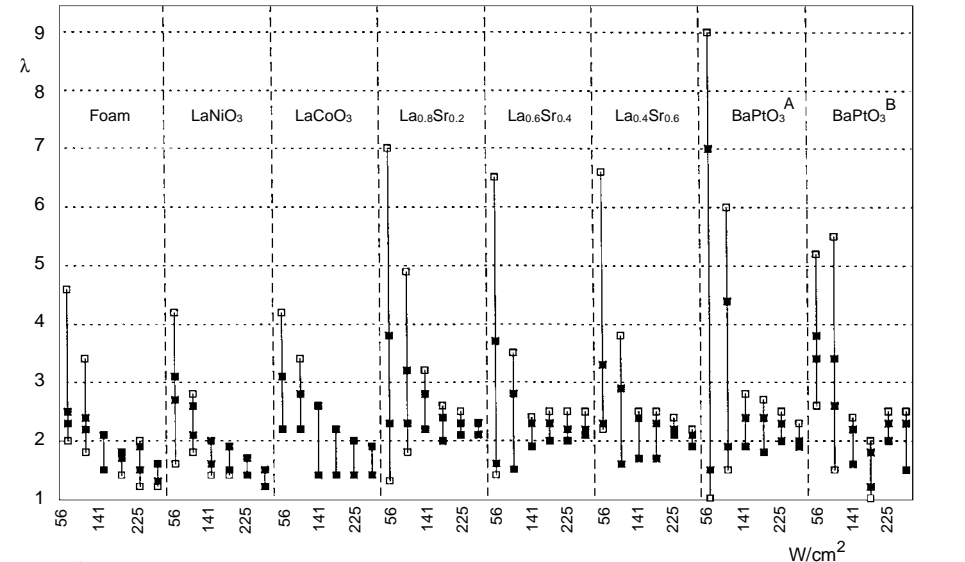| Sample	ml O_2/g	t_{max}, °C
$LaCoO_3$	4.8	103
$La_{0.8}Sr_{0.2}CoO_3$	4.9	137
$LaNiO_3$	4.8	116
$BaPtO_3^B$ (1.2 wt.,%)	5.1	116

FIG. 5
Dependence of the λ interval width on the burner capacity (W/cm^2) for the ceramic foam and the catalysts examined (see Table I). Points $\square$ denote the intervals in which the catalyst was working within the limits of 1 000 ppm of CO and maximum catalyst temperature 1 200 °C; points $\blacksquare$ denote the limits of λ in which the concentrations of NO$_x$ < 50 ppm and CO < 100 ppm were observed. The measurements were done for the burner capacities 56; 84; 141; 169; 225; 281 W/cm^2

Temperature-Programmed Desorption of Oxygen

We have tried to find a relation between catalyst activity and the oxygen bond strength determined from TPD experiments. The results of TPD of oxygen are shown in Table III. Total amount of oxygen desorbed from the catalysts was practically the same for all samples and temperature maximums of the desorption curves did not differ very much, either. Thus, TPD of oxygen did not give any important information that could be in relation to the catalyst activity.

Thermal Stability of the Catalysts

Though perovskite should be stable at high reaction temperatures[2], there were indications in our experiments (change of catalyst color) that the perovskites used turn into other components by the influence of high reaction temperature. For example, deep blue color of the $La_{0.2}Sr_{0.8}CoO_3$ catalysts or dark brown color of the $LaMnO_3$ catalyst became lighter in some parts of the catalysts after the combustion experiments. The lightest catalyst colors were observed in the center of the bottom layer of the catalysts. Using the JEOL electron microprobe instrument, we analyzed the composition of three

TABLE IV
Catalyst composition (mole %) at three places of the catalysts examined after the combustion of methane

Element	$La_{0.2}Sr_{0.8}CoO_3$[a]			$LaMnO_3$[b]			Foam
	s	b	u	s	b	u	
Al	47.1	63.6	77.7	69.9	74.6	83.5	51.5
La	4.3	8.3	3.6	4.0	6.1	1.6	–
Sr	23.2	13.0	7.0	–	–	–	–
Co	24.4	12.3	11.7	–	–	–	–
Mn	–	0.1	–	4.2	0	0.4	0.4
Si	–	1.2	–	–	9.3	4.4	25.6
Zr	–	0.5	–	11.1	8.2	9.0	7.0
K	–	0.1	–	–	0.2	–	0.9
Ca	–	0.1	–	0.3	0.2	–	2.9
Ce	–	0.4	–	–	–	–	0.7
Fe	–	0.2	–	0.6	1.0	1.0	1.5

[a] La : Sr : Co in Side 0.17 : 0.95 : 1, in Bottom 0.67 : 1.05 : 1, in Upper 0.3 : 0.6 : 1. [b] La : Mn in Side 0.94 : 1, in Upper 4 : 1.

samples taken from the $La_xSr_yCoO_3$ and $LaMnO_3$ catalysts (after the combustion experiments) in three locations: at the side, at the bottom center and at the upper center of the catalysts. The results are given in Table IV. Though it is necessary to consider the results very carefully (with respect to the possible non-uniform distribution of the catalyst particles and small area of analyzed sample found by electron microprobe – 0.01 mm^2), it is evident that the ratio of components in the $La_{0.2}Sr_{0.8}CoO_3$ perovskite at various places of the catalysts significantly differs. While the (La + Sr)/Co ratios of the sample from the side of the catalyst and from the upper central part of the catalyst approach the theoretical value, the sample taken from the bottom center of the catalyst showed a substantial increase in the (La + Sr)/Co ratio. The finding indicates a transformation of the perovskite and, possibly, its reaction with the support. Similar consideration can be done in the case of the $LaMnO_3$ perovskite. Both examples support the idea that thermal stability of perovskites is not sufficiently high at temperatures around 1 200 °C. Evidently, for the high-temperature combustion of methane, it will be necessary to study more thermostable materials, such as hexaaluminates.

CONCLUSIONS

The effect of the presence of active components (perovskites) in the ceramic foam on the composition of combustion products was examined. It was found:

1. The higher the catalyst activity, the wider the working range of an air excess λ in which a burner can work and the more stable the combustion process.

2. The pure ceramic foam and the foam-supported $LaNiO_3$ perovskite were working in the narrowest range of the air excess.

3. The effect of the $La_xSr_yCoO_3$ perovskite composition: Of the set of the catalysts with x/y = 4; 1.5; 0.66, the catalyst with x/y = 1.5 was the most active.

4. Perovskite $BaPtO_3$: More active catalysts for methane combustion were obtained with lower concentrations of perovskite in the ceramic foam (0.3 wt.%). Methane was oxidized with a very high excess of air (the burner worked reliably even at catalyst temperature of 500 °C).

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